COLOUR CENTRES IN PENTAHYDRATE CRYSTAL OF SODIUMTHIOSULPHATE

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ABSTRACT. It has been observed that pentahydrate crystals of sodium thiosulphate develop a yellow coloration after a few hours of irradiation by X-rays. Spectrophotometric analysis revealed that the coloured crystal has an absorption maxima at about 400 mμ. Even when kept in darkness, the crystal loses its coloration at a rate depending on the temperature. For example, at –5°C the colour persists for about 15 days without any appreciable bleaching and at 29°C it persists for 36 hours with a lot of bleaching.

The induced coloration disappears rapidly when the crystal is exposed to monochromatic radiation of a wave-length lying in the region of its absorption band. A new absorption band at about 1000 mμ is developed after bleaching of the crystal in complete darkness, whereas two new absorption bands, one at 1000 mμ and the other at about 580 mμ, the F′ band, appear after bleaching the coloured crystal by light of a wave-length lying in its X-ray induced absorption band.

INTRODUCTION

The study of the physical properties of crystals, which have been coloured either by exposure to X-rays, or cathode rays or by stoichiometric excess of the alkali metals, occupies an interesting place in the solid state physics. It appears that the coloration of crystals of alkali halides by cathode ray bombardment and subsequently by X-ray irradiation, was first observed by Goldstein (1896). Pohl (1937, 1938) gave the name of F band to the absorption band in the visible region developed in these crystals and ascribed the absorption to the production of absorbing centres in the crystals, which they called F centres (from the German word Farbzentren or colour centres).

Molnar (Seitz, 1946) observed that the coloration produced tends to a saturation value depending on temperature, the nature of the crystal and the intensity of the X-ray beam and that besides the F band, a new absorption band (called the V band) on the ultra-violet side of the F band and another (called the M band) on its infra red side are also produced by X-ray irradiation.

The F band is also induced in alkali halide crystals when they are heated in an atmosphere of the alkali metal vapour and then cooled rapidly to room temperature (*i.e.*, quenched). If instead of quenching, the crystal is cooled slowly after heating, an additional absorption band is observed and this is probably due to the formation of colloidal aggregates of the excess alkali metal (Hirschlaff,

1938). This additional absorption band lies between 550—600 mμ in NaCl depending on the size of the colloidal aggregates, the wavelength of the peak of the absorption band increasing with the size of the colloidal aggregates. The crystal appears blue by transmitted light.

Besides the coloration of alkali halides, the coloration of a few other crystals like that of chrome-alum (Braun, Many and Simchen, 1954), BaF_2 and CaF_2 (Smakula, 1950), etc. by X-ray irradiation, has been observed and studied. It appears that no previous worker has studied the coloration effects in sodium thiosulphate crystals by X-ray irradiation and therefore the present investigation has undertaken to study this phenomenon.

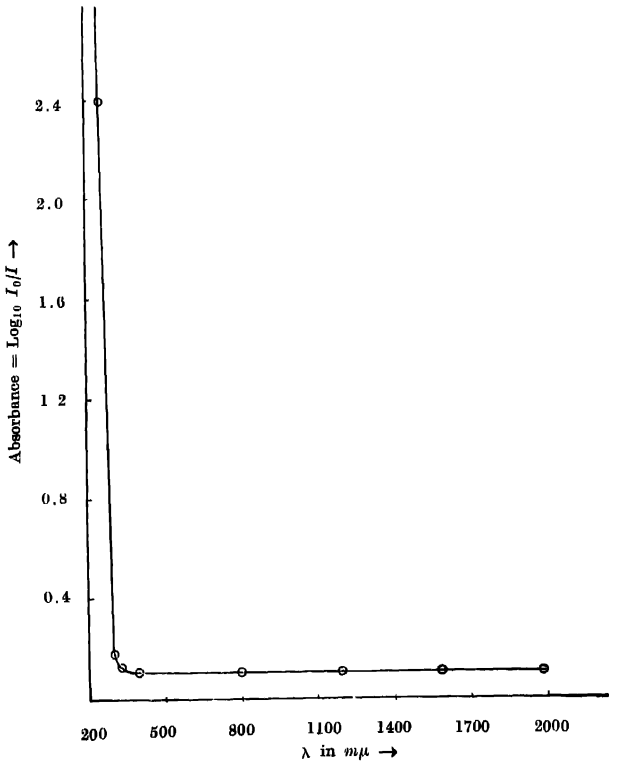

Fig. 1.

EXPERIMENTAL

Pentahydrate crystals of sodium thiosulphate were prepared in the laboratory from saturated solutions of Merck's sample of the salt in distilled water. The single transparent crystal was cut to the suitable size (2.0 cm × 1 cm × 0.5 cm) so as to fit in the cell holder of the Beckmann's Du model spectrophotometer. The transmittance of the unexposed and uncoloured crystal was first measured in the wavelength region 200 mμ to 2000 mμ Figure 1 shows the plot of the absorption of the crystal calculated from the measured transmittances.

The crystal was then irradiated for about 5 hours at room temperature (about 20°C) by unfiltered radiation of a copper target emerging through a beryllium window, the tube current being 8 mA at 50 KV The crystal developed a yellow coloration Its transmittances for different wavelengths were measured immediately after completion of irradiation and Curve 1 of figure 2 shows its

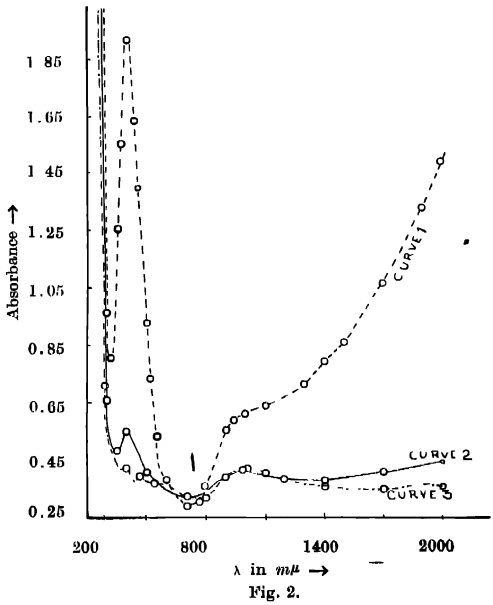

Fig. 2.

absorption calculated from the transmittance data. Curves 2 and 3 of figure 2 show its absorption in different wavelength regions observed after the crystal had been in dark at room temperature for five days and 54 days respectively.

It has also been found that the coloured crystal can be bleached by irradiation by a light of wavelength in the region of its absorption band. A second crystal was coloured by X-ray irradiation and its absorption curve (curve 1 of figure 3) was obtained immediately afterwards. The coloured crystal was then irradiated by light of the wavelength in the absorption band (*i.e.*, 405 mμ) for about 7 hours by placing it in the monochromated beam of 405 mμ in the DU model of Beckmann

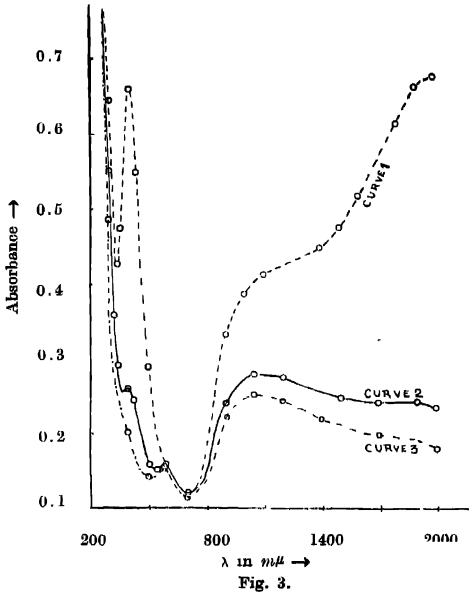

Fig. 3.

spectrophotometer. Table I is the observation for such irradiation. Curve 2 of figure 3 shows the extent of bleaching effected by exposure to light of wavelength in the region of its absorption band. The crystal was then left in dark at room temperature for 15 days more and Curve 3 of figure 3 shows its absorption after this period.

DISCUSSION OF RESULTS

It is clear from figure 1 that unexposed, colourless and transparent single crystals of sodium thiosulphate have negligible absorption in the region 300 mμ to 2000 mμ and perhaps beyond 2000 mμ also. After irradiation by X-ray the crystal is coloured and this coloration is due to an absorption band at about 400 mμ. From Curve 1 of figure 2 there is an indication of the presence of another band beyond 2000 mμ. Measurement could not be extended beyond 2000 mμ on

account of the non-availability of an infra red spectrophotometer. I shall call the absorption band at 400 mμ as the F band and that beyond 2000 mμ as the M band corresponding to the F and M bands developed in alkali halide crystals. The mechanism of the production of the colour centres responsible for these absorption bands are probably the same as that for alkali halide crystals, namely, the trapping of electrons and holes produced by energetic photo-electrons released by the impact of X-ray photons.

Curve 2 of figure 2 shows that the F and M centres are not stable but decay with time even in complete darkness probably due to thermal impacts. Those curves also show that while F and M bands are bleached almost completely, a new absorption band appears at about 1000 mμ. This is most likely due to the gradual drifting of the trapped electrons in the F and M centres to centres of greater stability.

Curve 3 of figure 2 shows that after 54 days the F and M bands are almost completely bleached while the band at 1000 mμ still persists together with the formation of a band at about 460 mμ which may be ascribed either to the formation of colloidal aggregates during the process of bleaching or to the drifting of the trapped electrons to centres of greater stability. After the above process of self-bleaching, the crystal still retains a faint bluish tinge.

Curve 1 of figure 3 is the absorption curve of another crystal of sodium thiosulphate coloured by X-ray irradiation. The crystal was then irradiated with light of wavelength 405 mμ, and the resulting decrease in its absorption is given in Table I. The increase in per cent transmittance with time has been plotted in figure 4. It is seen that in this case also the F and M bands are bleached just

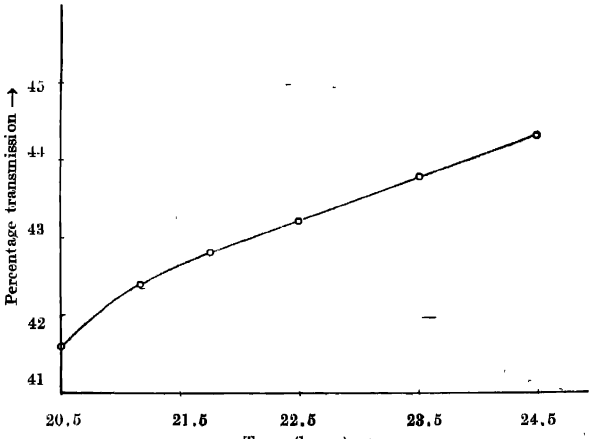

Fig. 4.

as when the coloured crystal is left in darkness for a long time; but in the present case the bleaching time is much smaller In this case also a new band at 1000 mμ and another at 580 mμ appear after bleaching. I shall call for the present the band at 580 mμ, the F′ band. This F′ band lasts for a much longer time when the crystal is left in darkness.

The number of F centres per c.c. formed in the crystal as a result of X-ray irradiation was calculated from the equation (Pohl, 1937)

$$N_0 = 1.31 \times 10^{17} \frac{n_0}{(n_0^2+2)^2} K_{max} H. \quad \ldots \quad (1)$$

Where, N_0 is the number of colour centres per unit volume.

n_0 ,, ,, refractive index of the crystal = 1.5

K_{max} ,, ,, absorption constant for the band maxima in cm^{-1}

H ,, ,, half width of the band in ev

The values of the number of the colour centres per c.c. present in the crystal at various stages have been calculated and are given in tabular form in Table II.

The pentahydrate crystal of sodium thiosulphate, $Na_2S_2O_3+5H_2O$, has a complex structure while the alkali halide crystals have relatively much simpler structure. Further studies on other physical properties associated with the formation of colour centres by X-ray irradiation, are necessary before venturing to explain all the observations reported above.

TABLE I

Time (hours)	% Transmission	Absorbance
0	24.4	613
1	26.6	.575
Dark interval for 19½ hours		
20½	41.6	.381
21⅓	42.4	.373
21¾	42.8	.369
22½	43.2	.364
23½	43.8	.358
24½	44.3	.354
Dark interval for 22 hours		
46½	52.2	.282
48	52.7	.278
48½	52.9	.276

TABLE II

Fig.	Curve	K_{max}	H	N_0
	1	7.70	1.01	84.5×10^{15}
2	2	2.21	41	$9.85 \times$ „
	3	1.67	.12	$2.20 \times$ „
	1	3.05	.59	19.57×10^{15}
3	2	1.20	.16	$2.07 \times$ „
	3	.92	0	$0 \times$ „

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